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MAGNETIC BEHAVIOUR OF THE CUBIC $La(Fe,Al)_{13}$ COMPOUNDS

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The magnetic properties of the cubic $NaZn_{13}$ type pseudobinary compounds $LaFe_xAl_{13-x}$ were studied in the temperature range T=4.2 - 300 K by means of ^{57}Fe-Mössbauer spectroscopy, magnetization and zero-field susceptibility measurements. The compounds $LaFe_xAl_{13-x}$ show a rather peculiar concentration dependence of the type of magnetic ordering as well as of the ordering temperature.

1. Introduction

$LaCo_{13}$, which is strongly ferromagnetic, is the only compound among 45 binary systems consisting of a rare earth element (R) and one of the metals Fe,Co or Ni (T) with the cubic $NaZn_{13}$ type of structure. Kripyakevich et al.[1] showed that the cubic $NaZn_{13}$ type of structure can be stabilized in other binary rare earth transition metal systems (R-T) by substitution of Si for part of the transition metal T in RT_{13}. Previously we have studied $LaFe_xSi_{13-x}$ [2] in the concentration region $10.5 \leq x \leq 11.5$. Only in this region single phase samples were obtained. In the present investigation we show that the structure stabilization occurs over a much wider concentration range when part of the transition metal T is substituted by Al. We have studied the magnetic properties of $LaFe_xAl_{13-x}$ by means of ^{57}Fe-Mössbauer spectroscopy, magnetization and temperature-dependent zero-field susceptibility measurements.

2. Experimental

The samples of the compounds $LaFe_xAl_{13-x}$ were prepared by argon arc melting of the appropriate amounts of the starting materials and vacuum annealed for about 10 days at T=1200 K. The samples were investigated by means of X-ray diffraction. Single phase samples of the cubic $NaZn_{13}$ type of structure were obtained in the concentration range $6 \leq x < 12$. For $x < 6$ a contamination with compounds of the tetragonal $ThMn_{12}$ structure is observed in the samples. Microscopic measurements indicate besides the $NaZn_{13}$ type of structure a so far unidentified second phase for $x \geq 12$.

The magnetic properties of these samples were determined by means of an adapted Faraday method in the range T=4.2 - 300 K using magnetic field strengths up to 1.8 T. The temperature dependence of the zero-field susceptibility has been determined with a sensitive pendulum magnetometer in the same T-range.

The ^{57}Fe-Mössbauer spectra were obtained by means of a standard constant-acceleration type spectrometer by using a ^{57}Co-Rh source.

3. Results

The shape of the magnetization versus temperature curve for

$x \leq 11.2$ is typical for a ferromagnet. The values for the saturation moment per iron atom at T=4.2 K (μ_s) and the values of the Curie temperature (T_c) are listed for the various compounds in Table 1 and plotted in fig. 1.

Table 1
The lattice constant a, T_c and μ_s determined from magnetization measurements and T_c' and $\bar{H}_{eff}$ determined from Mössbauer spectrometry of the compounds $LaFe_xAl_{13-x}$.

x	a(Å)	T_c(K)	$\mu_s(\mu_B/Fe)$	T_c'(K)	H_{eff}(T)
6	11.93	-	0	65	12.0
7	11.86	-	0	55	12.0
7.5	-	-	-	70	-
8	11.80	138	1.02	126	14.5
9	11.74	237	1.47	238	19.0
10	11.67	250	1.66	250	22.0
11	11.61	195	2.00	190	26.5
11.8	-	-	0.1	-	-
12.0	-	-	1.0	235	26.0

The saturation moment increases from $\mu_s \approx 0\ \mu_B$ for x = 7 to $\mu_s \approx 2.0\ \mu_B$ for x = 11. For x > 11 the magnetization is strongly decreasing to about $\mu_s \approx 0.1\ \mu_B$/Fe for x = 11.8. However for x = 12.0 $\mu_s \approx 1\ \mu_B$/Fe is measured. The Curie temperature (T_c) determined from magnetization measurement increases with increasing x and after reaching a maximum for x = 9.5 it decreases. For x > 11 it was impossible to determine T_c in this way.

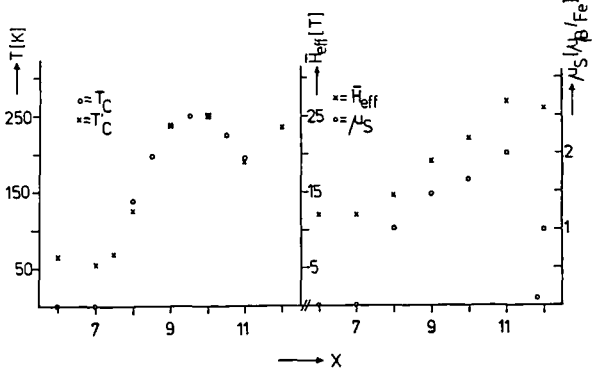


Fig.1. Concentration dependence of the Curie temperature, saturation moment μ_s and mean magnetic hyperfine field $\bar{H}_{eff}$ in $LaFe_xAl_{13-x}$

In fig.2 we have plotted the temperature dependence of the zero-field susceptibility for x = 11.2, 11.5, 11.8 and 12.0 respectively. The shape of the curve as found for x = 11.2 is characteristic for x < 11.2, indicating a sharp transition from ferromagnetic to paramagnetic behaviour. However a drastic change in the temperature dependence of the susceptibility is observed for x > 11.2.

The Mössbauer spectra obtained at T=4.2 K are shown in fig.3. The contribution of the unidentified second phase in the spectrum of $LaFe_{12}Al$ is clearly observed and the outermost lines of this contribution are indicated by arrows in fig.3. The unidentified phase

(≈ 40% of the sample) remains magnetically ordered at T=238 K as is shown in fig.4, while the other part of the sample is in the paramagnetic region. It is obvious that the spectrum of the sample with a nominal composition $LaFe_4Al_9$ really belongs to the compound $LaFe_4Al_8$ which crystallizes in the $ThMn_{12}$ type of structure [3]. The mean hyperfine fields deduced are listed in Table 1 and have been plotted in fig.1. The mean hyperfine field shows the same concentration dependence as the saturation magnetization from x = 11 to x = 8. However, for lower values of x, the mean hyperfine field levels off to the value observed for $LaFe_4Al_8$ ($ThMn_{12}$ structure), which compound orders antiferromagnetically [3]. The values of the magnetic ordering temperature (T_C') defined as the temperature at which the hyperfine splitting of the Mössbauer spectrum disappears are listed in Table 1 and also plotted in fig.1. A remarkable increase of T_C' for x = 12 has been observed after a decrease from T_C' = 250 K for x = 10 to T_C'=190 K for x = 11.

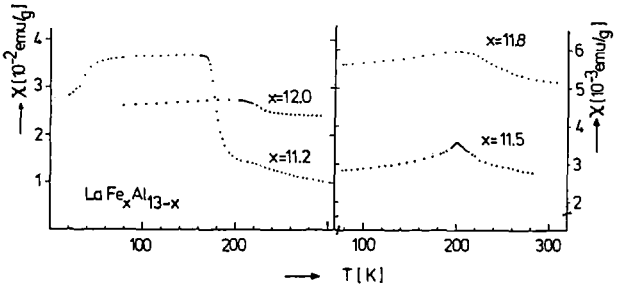


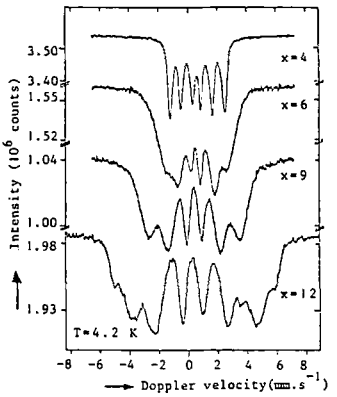
Fig.2. Temperature dependence of the zero field susceptibility χ_o in $LaFe_xAl_{13-x}$.

4. Discussion

The heat of alloying between La and Fe is positive [4]. As a consequence a stable La-Fe intermetallic does not exist. A minimum amount of Al will be required to lead to a pseudo-binary compound of a negative heat of formation and in addition form a suitable structure to accomodate the size of each of the three constituent atomic species.

In the compounds $LaFe_xAl_{13-x}$ the moment per Fe atom decreases with decreasing Fe concentration and behaves according to expectation for $8 \leq x \leq 11$. However, for $x \leq 7$ no net magnetization has been found at T=4.2 K while a magnetic hyperfine splitting is still observed in the Mössbauer spectrum. We believe that the loss of the net magnetization for $x \leq 7$ is due to formation of a spin glass, which means that for decreasing Fe concentration the ferromagnetic exchange interaction is decreasing faster than the antiferromagnetic one. For $x < 6$ the $ThMn_{12}$ type of structure becomes favoured. The composition of the compound formed is $LaFe_4Al_8$, which orders antiferromagnetically [3]. It is interesting that at the low Fe concentration region not only the antiferromagnetic exchange interaction becomes relatively strong, as in $LaFe_4Al_8$, but also the magnetic hyperfine field approaches the value observed for $LaFe_4Al_8$ [3].

In the high Fe concentration region the susceptibility measurements indicate that the pseudo binary compound is changing from entirely ferromagnetic ordering for x = 11.2 to an antiferromagnetic ordering for $x \geq 11.5$. This picture is qualitatively consistent with the very low magnetic moment observed for x = 11.8 while still a large hyperfine field is observed at the Fe-site. The increase of the



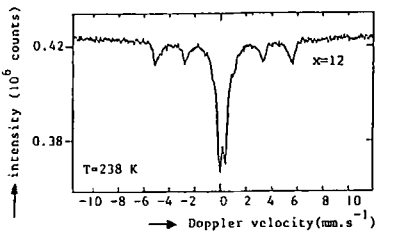


Fig.3. Mössbauer spectra at T=4.2 K for $LaFe_xAl_{13-x}$.
Fig.4. Mössbauer spectrum at T=238 K for $LaFe_{12}Al_1$.

magnetic moment for x = 12 is due to the large contamination of the sample with the so far unidentified second phase.

The opposite concentration dependencies of T_C and magnetic moment (as observed for $10 \leq x \leq 11.2$) were claimed to be associated with the anomalous thermal expansion below T_C found in Invar type alloys[5] and is also observed earlier by us in the compounds $LaFe_xSi_{13-x}$[2]. In these latter compounds we have observed a cusp like anomaly near T_C in their temperature dependence of the resistivity. Similar measurements on the present samples are in progress. The weakening of the overall ferromagnetic coupling for the compounds in the range $10 \leq x$ $x \leq 11.2$ can be understood in terms of the site occupation of the Fe atoms in the $NaZn_{13}$ crystal structure in conjunction with the lattice constant decreasing with increasing iron content. Denoting the two Fe sites by $Fe^{(1)}$ and $Fe^{(2)}$ in the hypothetical compound $LaFe_{12}{}^{(1)}Fe_1{}^{(2)}$, an increasing Fe concentration in $LaFe_xAl_{13-x}$ will lead to a larger occupation of both sites and hence to a larger occupation of the $Fe^{(2)}$ site. This site is characterized by a rather low Fe-Fe nearest neighbour separation and by a nearest neighbour configuration consisting of 12 Fe atoms. The $Fe^{(2)}$ nearest neighbour configuration is in several respects not much different from that of Fe atoms in γ-Fe. In the latter antiferromagnetism prevails and this may explain why one can expect an increasing antiferromagnetic interaction by filling more of the $Fe^{(2)}$ sites in $LaFe_xAl_{13-x}$.

The increase of the ordering temperature for $x > 11.2$ is not yet understood.

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